

# EDGEWOOD

## CHEMICAL BIOLOGICAL CENTER

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### CHEMICAL CHARACTERIZATION OF THE PYROTECHNICALLY DISSEMINATED KM03 RED PHOSPHORUS FLOATING SMOKE POT

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14. ABSTRACT The United States Marine Corps Floating Smoke Pot (FSP) MK 7 MOD 0 Program was established to redesign the previously fielded M4A2 Hexachloroethane (HC) Smoke Pot. Although the HC pots were extremely effective as an obscurant, there were safety concerns from a manufacturing and an operational perspective. Red phosphorous (RP) has been widely used in screening applications and was chosen as a replacement for the smoke payload. The smoke payload contained within the FSP MK 7 (KM03 pot) is a specific formulation that has been developed by Diehl BGT Defence GmbH and Co., KG (Überlingen, Germany). Before an item is type classified, data must be collected and evaluated for the item's Health Hazard Assessment (HHA) and/or Life Cycle Environmental Assessment (LCEA). This is accomplished by performing chemical and environmental characterization of the disseminated smoke. The data suggest RP floating smoke pots do not create additional risks upon dissemination, and the products are generally found to be less hazardous than the HC smokes. Combustion products, inorganic anions and cations, particle size, volatile organic compounds, and aquatic toxicology were all evaluated. The greatest concern for the current replacement smokepot program would be the high levels of phosphine that were observed during long term storage.					
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## **PREFACE**

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Records were maintained in official U.S. Army Edgewood Chemical Biological Center (ECBC) Notebooks in the Life Sciences Official Archives and/or in the Technical Library. Studies were conducted under and in compliance with current good laboratory practices (GLP). The performance of this study was consistent with the objectives and standards in "Good Laboratory Practices for Non-clinical Laboratory Studies" (21 CFR 58, Food and Drug Administration, U.S. Department of Health and Human Services, April 1988).

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# CHEMICAL CHARACTERIZATION OF THE PYROTECHNICALLY DISSEMINATED KM03 RED PHOSPHORUS FLOATING SMOKE POT

## 1. INTRODUCTION

The use of smokes and obscurants has historically been important to the military in various applications. Concealment, blinding, deception, and training are some examples of these applications.<sup>1</sup> The United States Marine Corps Floating Smoke Pot (FSP) MK 7 MOD 0 Program was established to satisfy the need of redesigning the previously fielded M4A2 Hexachloroethane (HC) FSP.<sup>2,3,4</sup> Although the HC pots were extremely effective as an obscurant, there were safety concerns from both a manufacturing and an operational perspective. One of these operational concerns was that venting of the HC smoke pots was recommended to reduce the risk of increased pressure.<sup>5</sup> In addition, the hexachloroethane/zinc chloride smoke created hazardous combustion products that were of toxicological concern and carcinogenic in nature.<sup>6</sup> Deaths have been directly attributed to the excessive inhalation of HC smoke.<sup>7</sup> Due to these concerns, it was decided that one of the Key Performance Parameters (KPP's) was to design a new smoke formulation that would retain operational efficiency and be the safest possible in terms of toxicity.

Red phosphorous (RP) has been widely used in screening applications where obscuration is achieved in various portions of the electromagnetic spectrum and has been typically deployed in either pots, grenades or 155 mm mortars.<sup>8</sup> Its chemical reactivity is considered intermediate to the stable black allotropic form and the highly reactive white allotrope. This, along with the fact that RP is the most common allotrope found in nature, made it a favorable choice for use in smoke payloads.<sup>8-10</sup>

Typically, before an item is type classified for full release, data must be collected and evaluated for input into the item's Health Hazard Assessment (HHA) and/or Life Cycle Environmental Assessment (LCEA). In addition to developing an effective smoke screening device, emphasis must also be placed on worker/user safety. One important portion of this data is to evaluate the combustion products observed after dissemination. In the current study, this was accomplished by performing chemical and environmental characterization of the disseminated smoke.<sup>11</sup> Suggestions and recommendations may therefore be made after making comparisons to established threshold limits as set by regulatory agencies, such as the American Conference of Government Industrial Hygienists (ACGIH). Decisions may be made to determine whether there are increased risks associated with the new item. Comparisons to previously reported data on the M4A2 HC smoke pot<sup>6</sup> may also be used to determine whether toxicological improvements have been met to satisfy the KPP of developing a low toxicity smoke.

The smoke pot payload (approximately 8 kg) contained within an FSP MK 7 is a specific formulation that has been developed by Diehl BGT Defence GmbH and Co., KG (Überlingen, Germany).<sup>12</sup> The pot is placed in a steel bucket (hobbock), surrounded by a nonflammable polyurethane foam and sealed.<sup>13</sup> The toxicity and combustion characterization of

RP smokes have been evaluated in the literature;<sup>8</sup> however, data is required to ascertain the toxicity risk associated with the current formulation. For example, phosphine is a highly toxic material<sup>14</sup> that has been shown to form during long term storage of these items, but has not been shown to appear at high levels during standard disseminations.<sup>15, 16</sup>

## 2. MATERIALS AND METHODS

### 2.1 Materials.

#### 2.1.1 KM03 Smoke Pots.

One pallet (18 total) of FSP MK 7 (Table 1) was transported to the Edgewood Chemical Biological Center (ECBC) from the Naval Surface Warfare Center, Dahlgren Division (NSWCDD), Virginia, and stored at the ECBC Engineering Directorate's Ammunition Storage Facility. Approximately 90% of the smoke composition is comprised of RP, cesium nitrate and zirconium. All smoke pots were kept as sealed units during storage to prevent the possible entry of moisture. Since the smoke composition is hygroscopic, moisture could induce the formation of gases, such as phosphine. On days of testing, one smoke pot (Figure 1) was delivered from the storage facility to a downrange open field testing site for sampling and analysis. At the start of the long term storage test, four smoke pots were transported to the Engineering Directorate's climatic controlled chamber for the monitoring of phosphine gas emissions.

Table 1. Smoke Pots Tested at ECBC

DODIC	KM03 / MK 7 Mod 0
NSN	1365-01-487-2843
Lot Number	DNM04L001-001
DOT Nomenclature	UN 0016 Ammunition Smoke
US Hazard Class	1.3G

#### 2.1.2 Ion Chromatography Reagents and Phosphine Mixture.

Sodium bicarbonate ( $\text{NaHCO}_3$ ) and sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) were purchased from Fisher Scientific. A seven anion stock standard used for calibration was purchased from Dionex (P/N 56933) (Sunnyvale, CA), which includes:  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ , and  $\text{SO}_4^{2-}$ . As recorded by the manufacturer's certificate of analysis, the concentrations of the anions in the stock standard were 19.9, 30.1, 100, 99.8, 100, 149, and 149 mg/L, respectively. Calibration standards were prepared by making dilutions of 2:1, 5:1, 10:1, 12.5:1, 25:1, 50:1, 100:1, 200:1, 400:1, and 1000:1.



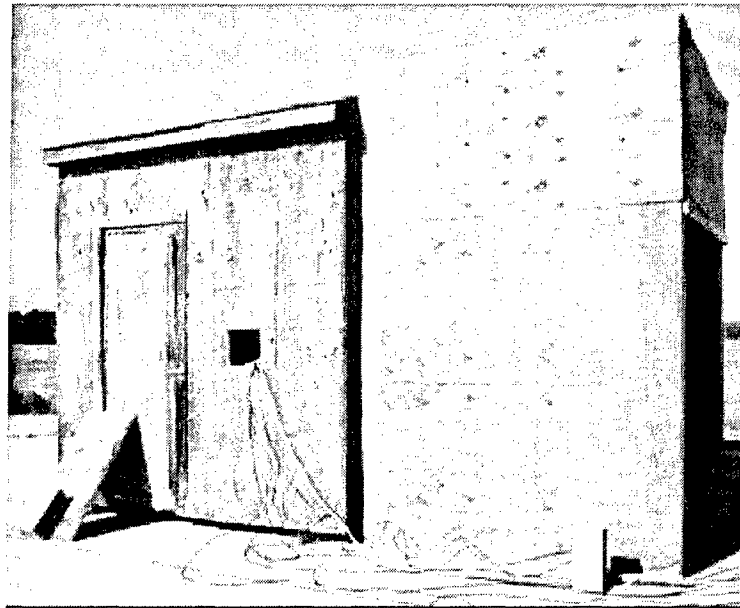


Figure 2. Field Setup Showing Shed and Tunnel for Dissemination of KM03 Smoke Pot

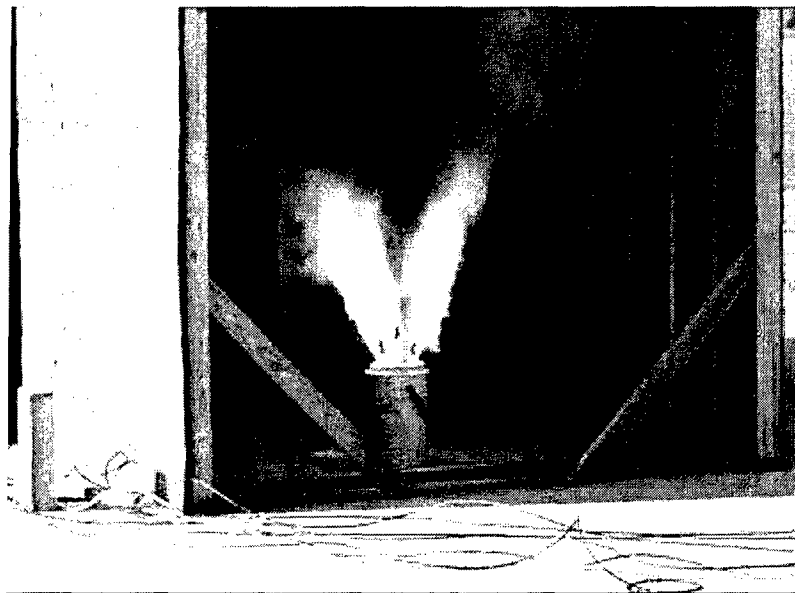


Figure 3. Initial Flame Burst from Dissemination of KM03 Smoke Pot

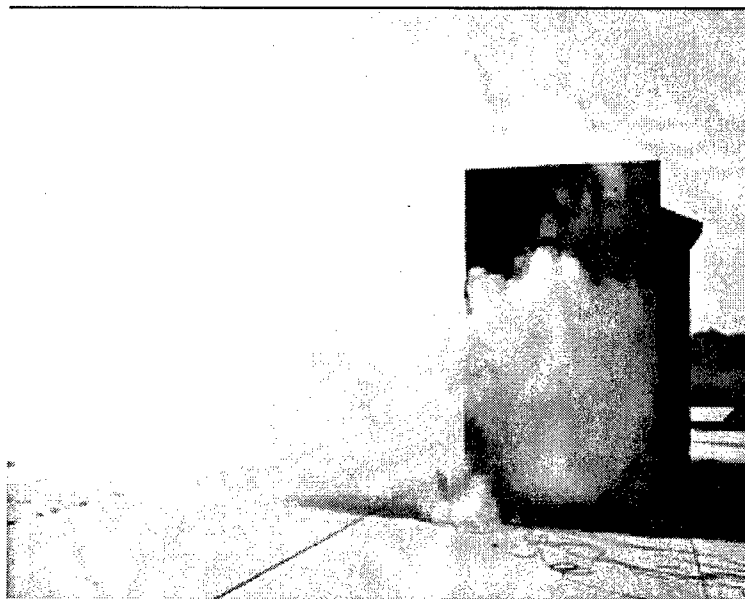


Figure 4. Smoke Production from the Dissemination of a KM03 Smoke Pot

Samples were collected inside the shed approximately four feet above the ground and at a distance of approximately 7-8 ft from the pot (Figure 5). At the conclusion of the test, care was exercised in removing the smoke pot due to the possible conversion of some red phosphorus into the more reactive white phosphorus. Figure 6 shows the smoke pot at the conclusion of a field test.

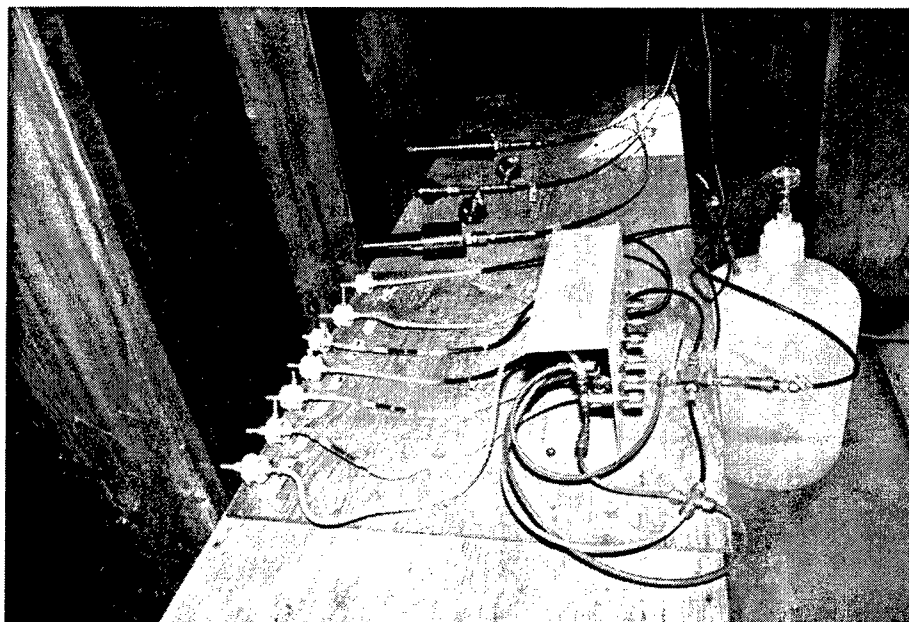


Figure 5. Sampling Equipment in Shed for Collection of Smoke Produced from the KM03 Smoke Pot



Figure 6. KM03 Smoke Pot Following Dissemination (scale = 12 in.)

### 2.3 Field Collection.

#### 2.3.1 Shed Concentration.

To determine the total aerosol concentration in the shed produced from one smoke pot, a 25 mm, HEPA A/E Glass Fiber Filter (GFF) pad (Gelman Scientific, Albany, NY) was used to collect the generated particulates. Samples were drawn with a vacuum pump at a flow rate of 8-10 L/min. The time duration varied depending on the concentration of smoke. Sampling began once the shed was visibly filled with smoke (usually within 1-2 min). Gravimetric analysis using a Mettler MT5 microbalance was used to determine the mass collected on the pad. Calibration of the balance was performed with American Society for Testing and Materials (ASTM) Class 1 weights. At the conclusion of the test, the filter holder assembly was sonicated and cleaned prior to the next dissemination.

#### 2.3.2 Particle Size Collection.

Cascade impactors (Sierra Instruments, Monterrey, CA) were used to monitor the particle size distribution of the generated smoke cloud. For each smoke pot, air was drawn from the shed through the impactor at 7 L/min (as specified by the manufacturer). GFF substrates were used to collect the particles on the stages. Two impactors were used for each dissemination. Gravimetric analysis using a Mettler MT5 microbalance was used to determine the mass collected on each stage of the two impactors. Generally, the total amount collected among all samples was kept below 100 mg to avoid the possibility of overloading the stages or clogging the slits of the impactor. This was controlled by adjusting the sampling time.



### 2.3.3 Volatile Organic Combustion Products (VOCs).

Smoke vapor samples were drawn and collected onto 10 mm multibed sorbent tubes (CDS Dynatherm Inc., Oxford, PA) (Part Number AO-06-2731) packed with equal portions of Tenax-TA, Carboxen 1000, and Carbosieve S111. Three sorbent materials were used to assure that both high and low molecular weight compounds would be trapped during the dissemination. Prior to their use, all sampling tubes were conditioned at 300 °C for 30 min with nitrogen flowing through them at 50 mL/min. Atmospheric blanks outside the sampling shed were collected from the surrounding air, but only before the first dissemination. Prior to each dissemination, three field blanks were initially drawn from the shed to collect background samples. During the dissemination, three additional tubes were used to sample the smoke cloud for VOC's. To prevent aerosols from passing into the tubes, GFF pads were attached to the front portion of each tube. Vacuum flows through the tubes were monitored with the pads attached to adjust for any resistance. Rates were set with valves and checked against a separate external flow-measuring device (Drycal, DC-Lite, Bios International, Butler, NJ). Initially, samples were drawn for 100 mL/min. Flow rates were later increased to 500 mL/min to assure that a sufficient quantity of air was drawn to detect lower concentrations of potentially toxic compounds.

Thermal desorption Gas Chromatography Mass Spectrometry (GC/MS) was used to analyze for VOC's collected on the tubes. Prior to injection onto the GC/MS, all field samples were concentrated within the thermal desorption system onto a trap (CDS Dynatherm Inc., Part Number AC-06-5223) containing the same three sorbents that were used during field collection. The thermal desorption system was a CDS Analytical ACEM 900 system and the GC/MS system was an Agilent 6890 gas chromatograph equipped with a 5973 mass selective detector. Separation conditions were followed according to the approved NIOSH Manual of Analytical Methods (NMAM) 2549 entitled "Volatile Organic Compounds (Screening)".<sup>18</sup>

### 2.3.4 Inorganic Gas Collection.

A 13-gal low-density polyethylene (LDPE) carboy was used as a vacuum reservoir (Figure 7) to collect for inorganic gases. A hole was drilled into the lid of the carboy and fitted with a PVC schedule 40 fitting. This fitting was sealed with a butyl rubber gasket. A Tedlar bag was attached to the inner lid portion of the Polyvinylchloride (PVC) fitting with a stainless steel band clamp and a pipe weld fitting to a 3/8 in. swagelok tube. A 47 mm filter housing was attached to the 3/8 in. swagelok tube protruding from the outer portion of the lid. When assembled, the bag had an opening through the lid and filter housing to the outer atmosphere. A 1/2-in. National Pipe and Thread (NPT) thread was tapped into the top portion of the carboy and a 1/2-in. male NPT-1/4 in. swagelok fitting was threaded into this hole. One end of a 1/4-in. LDPE line was attached to the 1/4 in. swagelok fitting (via double end shut off quick connects) and the other end was attached to a vacuum pump. When the pump was started, a negative pressure was created in the carboy thereby pulling atmospheric air through the filter into the bag. The length of sampling was approximately 5 min at 5 L/min.

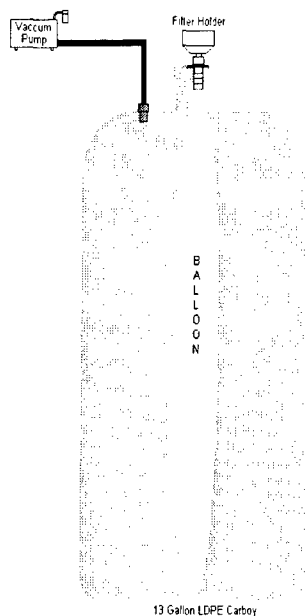


Figure 7. Experimental Design for Trapping Inorganic Gases

Gas samples were pulled from the carboy onto a compound specific detector tube (Kitegawa, Schaunberg, IL) using a Matheson portable gas sampling pump (Model 400). Concentrations were recorded by monitoring the colorimetric change observed on the sorbent material. Phosphine ( $\text{PH}_3$ ), hydrogen chloride ( $\text{HCl}$ ), hydrogen cyanide ( $\text{HCN}$ ), hydrogen fluoride ( $\text{HF}$ ), carbon monoxide ( $\text{CO}$ ), carbon dioxide ( $\text{CO}_2$ ), formaldehyde ( $\text{HCHO}$ ), nitrogen oxides ( $\text{NO}_x$ ), ammonia ( $\text{NH}_3$ ), and sulfur dioxide ( $\text{SO}_2$ ) were all monitored after each dissemination. Table 2 lists the Manufacturer's (Kitegawa) tube part numbers along with their respective measuring range.

### 2.3.5 Inorganic Anions and Cations.

Vacuum pumps were used to draw air samples from the shed onto three 25 mm, HEPA A/E GFF pads for each dissemination. Typically, several liters per minute were drawn for times greater than 10 min. Rates were set with valves and checked against a separate external flow-measuring device (Bios International, Drycal, DC-Lite).

Ion chromatography was used to analyze the components collected on the GFF pads. The instrumentation was a Series 4000i Dionex Ion Chromatograph (IC). For anions, a Dionex anion exchange column (IonPac AS4A-SC 4 x 250 mm, analytical) and guard column (IonPac AG4A-SC 4 x 50 mm) were used, and for cations, a Dionex cation exchange column (IonPac CS12A-SC 4 x 250 mm, analytical) and guard column (IonPac AG4A-SC 4 x 50 mm) were used. The isocratic separation was accomplished using a 1.7 mM  $\text{NaHCO}_3$ /1.8 mM  $\text{Na}_2\text{CO}_3$  mobile phase with a flow rate of 2.0 mL/min. Injections were made using an inert high pressure valve (Dionex P/N 038532), dual stacked, and air activated with 3 passages. Detection was accomplished using an anion self suppression (SRS) system with conductivity detection for anions and a cation self suppression (SRS) system with conductivity detection for cations.

Analytical methodology was followed according to the NIOSH approved method #7903 (Fourth Edition, 1994).<sup>19</sup>

Table 2. Kitegawa Part Numbers and Measuring Ranges for Tested Inorganic Gases

Inorganic Gas	Manuf Part Num	Meas Range(ppm)
NO <sub>x</sub>	8014-175U	0.5-30
PH <sub>3</sub>	8014-121SD	0.25-10
HF	8014-156S	1-30
NH <sub>3</sub>	8014-105SC	5-130
CO	8014-106S	10-250
HCN	8014-112SB	0.5-100
HCHO	8014-171SB	1-35
SO <sub>2</sub>	8014-103SE	0.25-10
HCl	8014-173SB	0.4-40

The GFF pads collected from the canister disseminations were placed in petri dishes and stored in a dessicator. After removal, gravimetric analysis was performed on the pads to determine the amount of residue collected. Each pad was placed into a separate 25 mL beaker and 2 mL of 1.7 mM NaHCO<sub>3</sub>/1.8 mM Na<sub>2</sub>CO<sub>3</sub> were added. Cation and anion analyses were performed on the same pad. The pads were shaken and allowed to sit for 1 hr. One additional blank pad was subjected to the same sample preparation conditions and used as the control.

#### 2.4 Aquatic Toxicology.

Smoke residue was collected using 47 mm HEPA GFF pads mounted in a filter housing attached to a vacuum line. Air was pulled through the filter at 6-8 L/min during the entire dissemination and clearance time. The filters were weighed before and after residue collection to determine total weight collected. The filters were placed in petri dishes and stored in a dessicator until needed for aquatic toxicity testing.

The smoke particles were small enough to embed and clog the filter before any visible residue could be seen. Removal of the residue for aquatic toxicity testing by scraping could not be done. The filters were placed into 50 mL of media and gently swirled to dissolve the residue off the pad to produce an extract. The pads were dried in an oven at 38 °C for 1 hr then allowed to stand at ambient temperature for an additional hour before being weighed. The difference between the filter pad weights before and after extraction was considered the nominal concentration in solution. During the extraction process, bits of pad were broken off and remained in the solution. The extract was not filtered to remove the pad particulate because the smoke particulate would also be removed. Instead, a correction factor was developed. Blank filter pads were subjected to the extraction procedures to determine the weight loss from pad deterioration. An average of 0.82 mg (n=5) of pad material was lost during the extraction procedure. A correction factor of 0.82 mg was subtracted from each of the total residue weights

extracted from each pad before determining the nominal concentration. The individual extracts were combined into one bulk sample and pH adjusted before being used in the toxicity testing. The smoke extract had an initial pH of 2.0 and was adjusted to 6.5 – 7.0 using 0.5 M NaOH. During these experiments, it was desired to determine the potential toxicity from the particulate effect and not from extreme pH conditions. The toxicity from low pH conditions in the described assays is known and is therefore not necessary to investigate further.

#### 2.4.1 Microtox (MTX) Assay.

The MTX assay<sup>20</sup> exposes bioluminescent marine bacteria (*Vibrio fischeri*, NRRL B-11177), to a sample of unknown toxicity, so that changes in the output of bioluminescent light by the bacteria may be measured as the means of determining the level of toxic effects on the bacterial organisms. Under proper test conditions, the reduction in light output is a direct indication of metabolic inhibition. The bacteria were cultured by Azur Environmental<sup>20</sup> and shipped in lyophilized form. The bacteria (stored frozen) were re-hydrated immediately before testing using the MTX Reconstitution solution. Individual assays were performed in a temperature-controlled photometer using glass cuvettes containing 1 mL of sample. For optimum accuracy in predicting toxicity, the bioassay must have a minimum of four dilutions exhibiting a dose response. At 5 and 15 min, the control and treatment groups were measured for light output. Data were analyzed using the MTX 100% test protocol software to determine the EC<sub>50</sub>, the effective concentration causing a 50% reduction in light output.

The smoke extract contained a high concentration of suspended materials (pad and residue). Suspended materials can interfere with the detection of light that is produced by the bacteria and yield unrepresentative results. Therefore, suspended solids were removed from samples by allowing the solids to settle before sampling the clear aqueous fraction for toxicity testing. Sample parameters (pH and salinity) were measured and adjusted as needed. The pH was adjusted to 6.5 - 7.0 as described above, and the salinity was adjusted to 2% by adding sodium chloride directly to sample. The extract was diluted with media to produce nominal concentrations of 157, 314, 628, 1256, and 2512 mg/L.

Quality Assurance/Quality Control (QA/QC) testing was conducted using zinc sulfate (ZnSO<sub>4</sub>) as a standard toxicant. Using a standard whose toxicity is well known confirms the health of the test organism, and also checks the performance of the entire MTX system. The acceptable toxicity range for the EC<sub>50</sub> value using the culture-lot of *Vibrio fischeri* used in these investigations was between 3 and 10 mg/L for ZnSO<sub>4</sub>, as prescribed by Azur Environmental.<sup>20</sup> If the test result for the EC<sub>50</sub> value of the ZnSO<sub>4</sub> standard was outside this range, a new standard was prepared and tested. If the standard result was still out of the range, a new batch of bacteria from the same culture-lot was prepared, and the ZnSO<sub>4</sub> was re-tested.

#### 2.4.2 Algal Assay (*Selenastrum capricornutum*).

Algal Growth Inhibition Assays were conducted according to the USEPA standard method using stock solutions of macro- and micronutrients prepared with ASTM Type I water.<sup>21</sup> Stock cultures of the unicellular green algae *Selenastrum capricornutum* were grown in 3- batches and taken during log phase growth for inoculation of test chambers. The initial algal

concentration was  $2 \times 10^4$  cell  $\text{mL}^{-1}$  per test chamber. The test chambers consisted of a glass screw top culture tubes containing a total volume 15 mL. The test design consisted of three replicates per treatment and control groups. Samples of smoke residue extract were diluted to the desired concentration using algal media to produce nominal concentrations of 125, 250, 500, 1000, and 2000 mg/L. The treatment and control groups were subjected to test conditions for 96 hr (static non-renewal). Following inoculation with algae, individual test chambers were randomly placed in an incubator at  $25 \pm 1$  °C, and exposed to 350 ft candles of continuous light. The chambers were shaken by hand twice daily. Cell density determinations were accomplished via the manual microscope counting method (hemocytometer) at 96 hr.

#### 2.4.3 Ceriodaphnia Assay (*Ceriodaphnia dubia*).

Ceriodaphnia Survival and Reproduction Assays were conducted according to the USEPA standard method.<sup>21</sup> The media for ceriodaphnia cultures consisted of 20% Perrier water and 80% reverse osmosis (RO) water. Ceriodaphnia were fed a mixture of *S. capricornutum* ( $6 \times 10^5$  cells/mL), and cerophyl extract (120  $\mu\text{g/mL}$ ). The algae were cultured for approximately 7 days before being harvested and fed to the ceriodaphnia at a concentration of approximately  $10^6$  cells/ mL.<sup>21</sup> Test chambers consisted of 30 mL plastic beakers containing a total of 15 mL of solution. Ten replicates of each treatment group and control were prepared, with each replicate containing one ceriodaphnia. The test media was renewed and fresh food added daily, for 7 d. Mortality and reproduction were recorded daily. A diurnal light cycle was maintained at 16 h light:8 h dark. The light intensity was approximately 85 ft candles as measured at the top of the test chambers. The temperature was maintained at 25 °C. Ceriodaphnia were exposed to extracted smoke residue that was serially diluted with test media to obtain the nominal treatment concentrations of 16, 32, 63, 126, 251, 505, and 1004 mg/L. In previous testing (Anthony et al.),\* control groups were run using 100% extract from control pads to determine the effects from pad particulate in solution. It was determined that the pad material had no effect on ceriodaphnia reproduction.

#### 2.5 Long-Term Storage Test.

##### 2.5.1 Long-Term Storage Test - Experimental Design.

Four smoke pots, contained within their respectively sealed hobbocks, were placed directly inside the middle of a 12 ft x 7 ft x 8 ft (672  $\text{ft}^3$ ) static, climatically controlled aging chamber (Figure 8). The smoke pots were stacked as two groups of two and numbered 1-4. To sample the chamber air, a 1/4 in. OD stainless steel tube was run through the bulkhead of the chamber and was sealed at the inner and outer bulkhead with rubber stoppers.

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\*Anthony, J.S.; Davis, E.A.; McCaskey, D.A.; Haley, M.V.; Matson, K.L.; Crouse, C.L. *Chemical Characterization of the Pyrotechnically Disseminated XM2002 Bi-Spectral Smoke Canister*; U.S. Army Edgewood Chemical Biological Center: Aberdeen Proving Ground, MD, UNCLASSIFIED Report, unpublished data 2006.

The tube extended directly between the smoke pots (Figure 8). When sampling was not occurring, the outer portion of this tube was sealed with a cap. The long term storage timeline was calculated using the Arrhenius Relationship for accelerated testing. For the current accelerated aging test, the safest temperature was 167 °F. At this temperature, the natural aging from one year may be simulated in 1.625 weeks.<sup>22</sup> Therefore, to simulate 5 years, 8.125 weeks at 167 °F was required. The start date was September 07, 2005 at 14:35 hr, and the end date was November 03, 2005 at 1230 hr. Temperature remained constant during the entire length of the test.<sup>23</sup> Sampling of the air space in the chamber was conducted prior to the start of the experiment.

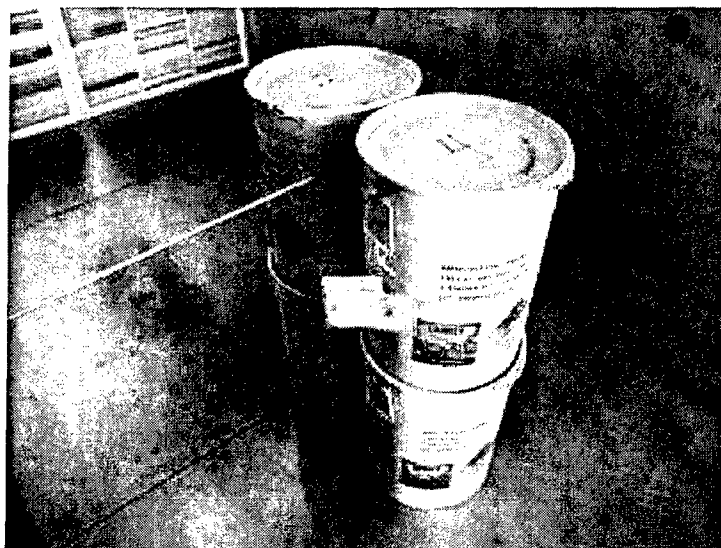


Figure 8. Four Smoke Pots in their Respective Hobbocks. Stacking in the chamber and placement of the sampling tube.

#### 2.5.2 Long-Term Storage Test - Chamber Sampling.

Sample collection and analysis was performed once a week. Gas from the chamber was pulled through the sampling tube with a 2-L Hamilton syringe (Hamilton Co., Reno, NV). A small fitting on the front of the syringe was closed, and the syringe was allowed to sit for approximately 30-60 sec to cool and return to ambient temperature. A latex tube was then placed on the fitting and opened to allow connection of the syringe to a magnahelix. This is used to measure the change in volume once the gas from the chamber was allowed to cool. The plunger was pushed until the magnahelix read 0 in. of water. The fitting on the front of the syringe was closed and the latex tube was connected to a tedlar 1-L bag (A-L Compressed Gas, Spokane, WA) where approximately 1 L of gas from the syringe was dispensed into the bag.

#### 2.5.3 Long-Term Storage Test - Analytical Methods.

##### 2.5.3.1 Phosphine Detector Tubes.

According to the air volumes predetermined by the manufacturer, samples were pulled from the bag onto a phosphine specific detector tube (Kitegawa) using a Matheson

portable gas sampling pump (Model 400). Concentrations were recorded by monitoring the colorimetric change observed on the sorbent material.

#### 2.5.3.2 Phosphine GC/MS Method.

The GC/MS was used to analyze for phosphine collected from the air samples. The GC/MS system was an Agilent (Palo Alto, CA) 6890 gas chromatograph equipped with a 5973 mass selective detector. Analytical separation conditions were followed according to the method described by Norman, et al.<sup>24</sup> Manual gas injections were made into a flash vaporization glass liner (4 mm i.d.) at 150 °C in split mode with a split flow of 6.4 mL/min with a total flow of 12.3 mL/min at constant pressure of 5.3 psi with a 2:1 split ratio. The detector transfer line was 300 °C. A 30 m x 320 µm i.d. J&W GS-Q column with helium carrier gas was used. A length of 30 cm x 250 µm i.d. J&W DB-624 column was connected to the end of the GS-Q column using a pressure fit connector and passed through the heated transfer line to the MS. The initial oven temperature was held at -20 °C for 1 min and programmed to 100 °C at 50 °C/min for 6 min. The MS used electron ionization at 70 eV in selective ion monitoring (SIM) mode. The three major ions and their respective relative intensities collected were m/z 31 (30), m/z 33 (30) and m/z 34 (100).

### 3. RESULTS

#### 3.1 Shed Concentration.

Over the duration of the study, the mean total particulate concentration in the shed was found to be 1856 mg/m<sup>3</sup> with a Standard Deviation (SD) of 1384 mg/m<sup>3</sup>. In this experimental design, strict controls were not implemented to maintain a stable or a uniform concentration within the shed. These controls were unnecessary during this open-aided test.

The burn time for each canister was recorded from the time of initial smoke production to the time at which the smoke generation had ceased. Many times at the conclusion of the test, the flame would still be lit, but there was no smoke being produced. Burn times ranged from 22-25 min. Each pot was also weighed prior to and after dissemination to determine the quantity of material disseminated from each canister. The percentage of smoke material disseminated from the pots was 64-66%. This percentage is based on a nominal smoke payload in each smoke pot of 16.31 lb (7.38 kg).<sup>25</sup>

#### 3.2 Particle Size.

Figure 9 depicts two cascade impactors that were sampled during one smoke pot dissemination. The GFF substrates are shown below each of the individual stages and are numbered from right to left as 1-8 and Final (F). As the aerosol is drawn through the impactor, the larger particles are deposited on the first few substrates and the smaller particles are deposited on the higher substrates. The final stage has no slits and functions as a filter to collect the remaining particulates that are not separated out among the other substrates.

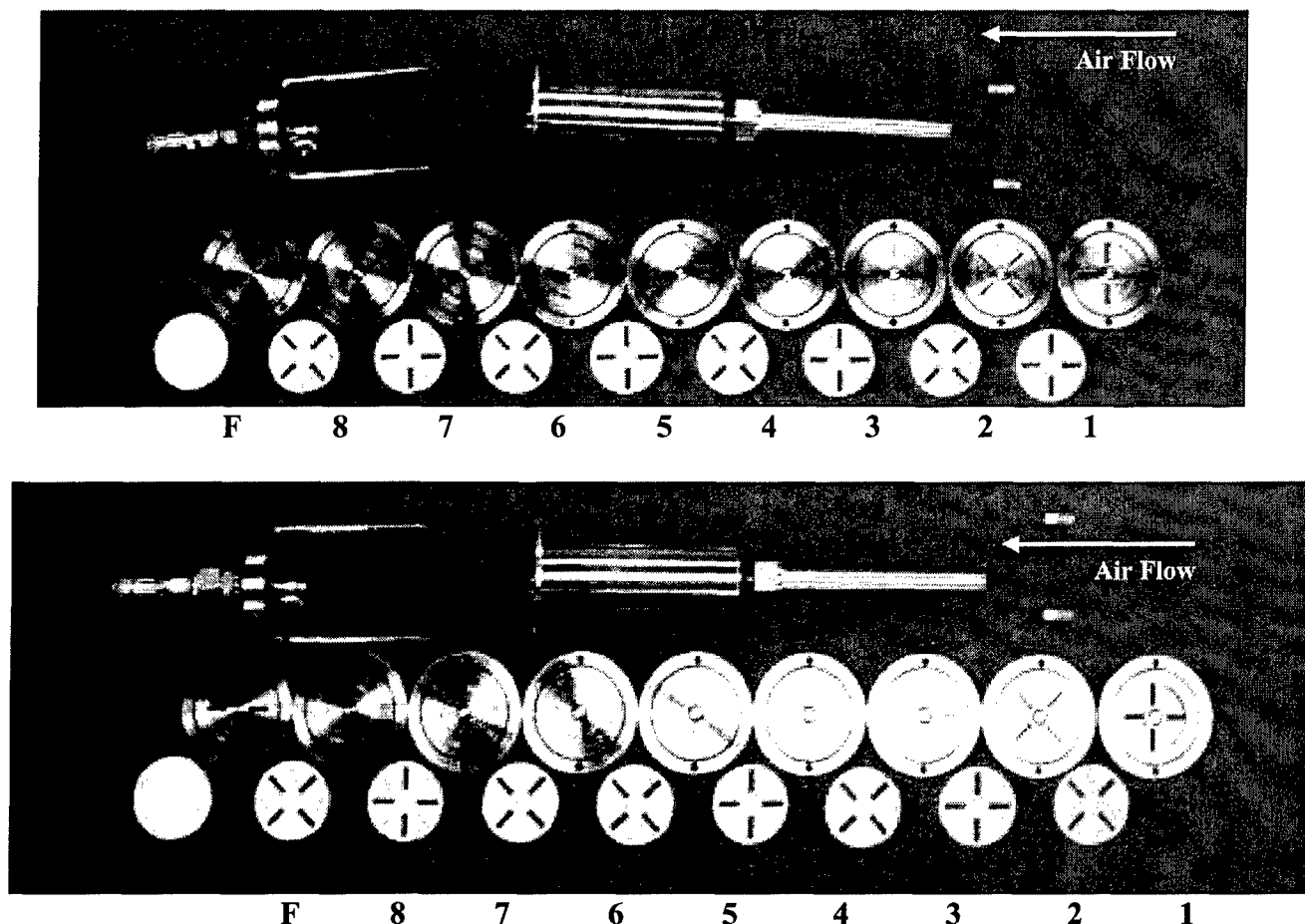


Figure 9. Cascade Impactors with GFF Substrates. Solid aerosol is visible on the pads following an experimental test

Figure 10 shows that a majority of the aerosol was visible on pads 6-8 with the highest impaction on pads 7 and 8. Prevalent impaction on these higher numbered stages infers that the particles are very small in size. After inspection, it was also observed that the collected material had a dark gray, "oily" appearance to it rather than a dry appearance. Table 3 shows an example of the raw particle size data that was accumulated from one dissemination. The cut-off diameters ( $D_p$ ) of the stages are shown and range from  $18\text{ }\mu\text{m}$  to  $0.32\text{ }\mu\text{m}$ . The sample weights for each stage were calculated by subtracting the tare weights from their respective gross weights. The cumulative total for the stages is calculated by summing the sample weights from the current and preceding stages. The respirable mass percentages were calculated using the current ACGIH model. Figure 11 is the graphical representation of the data in Table 3. The mass median aerodynamic diameter (MMAD), geometric standard deviation (GSD,  $\sigma_g$ ), and correlation coefficient ( $r^2$ ) for this dissemination were calculated from the regression data and are all shown in Figure 11. Table 4 shows all of the individual values for MMAD,  $\sigma_g$ , and respirable mass percentage calculated for each RP FSP dissemination with the mean values of  $0.65\text{ }\mu\text{m}$ , 1.83 and 98.2 %, respectively.



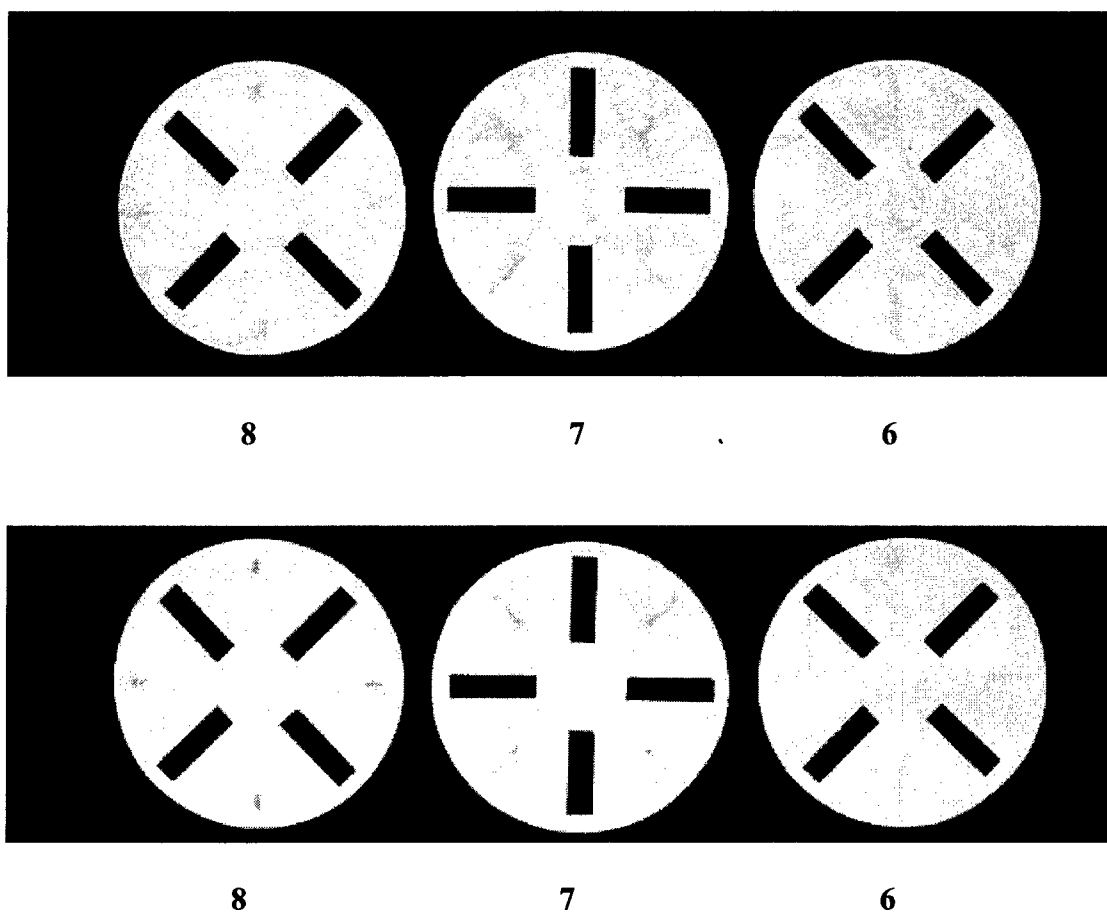


Figure 10. Closer Images of Substrates 6-8 from the Cascade Impactor after Dissemination from a KM03 Smoke Pot

Table 3. Data Accumulated from One Particle Size Analysis

stage	Dp	INPUT DATA			Cumulative	Respirable
	um	tare wt (mg)	gross wt (mg)	sample wt (mg)	Total (mg)	Mass %
F	na	94.2	99.9	5.7	5.7	9.484
8	0.32	84.5	96.5	12	17.7	19.967
7	0.53	83.8	108.5	24.7	42.4	41.091
6	0.95	84	100.2	16.2	58.6	26.641
5	1.7	84	85	1	59.6	1.452
4	2.65	84.9	85.4	0.3	59.9	0.251
3	4.4	84.1	84.4	0	59.9	0.000
2	11	85	84.8	0	59.9	0.000
1	18	84.3	84.5	0.2	60.1	0.000

98.886 %

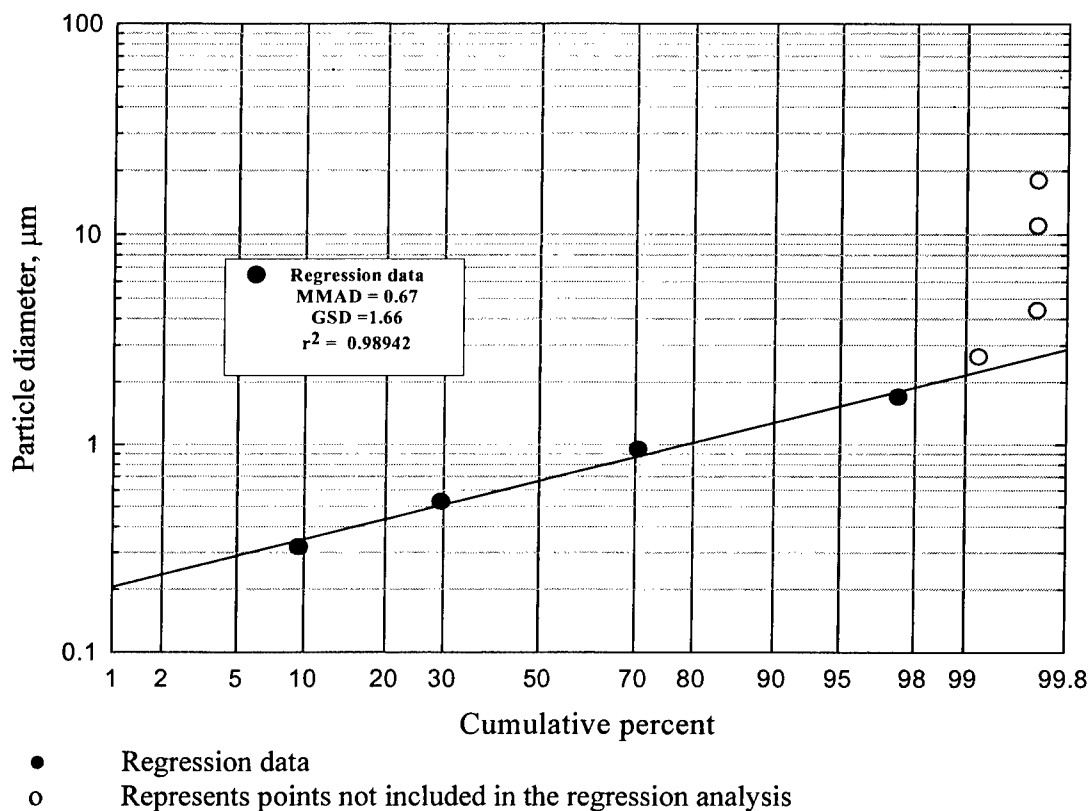


Figure 11. Particle Diameter ( $\mu\text{m}$ ) vs. Cumulative Percent

Table 4. Particle Size Analysis from Each RP FSP Dissemination

Dissemination Date	MMAD ( $\mu\text{m}$ )	$\sigma_g$	Respirable mass (%)
7/26/05	0.89	3.45	90.8
7/26/05	0.40	1.56	98.6
8/11/05	0.77	1.92	97.3
8/11/05	0.62	1.70	99.0
8/18/05	0.77	1.54	98.9
8/18/05	0.58	1.89	98.0
8/24/05	0.67	1.67	99.0
8/24/05	0.60	1.73	99.0
9/1/05	0.66	1.83	98.4
9/1/05	0.79	1.74	98.2
9/19/05	0.67	1.66	98.9
9/19/05	0.55	1.72	99.3
9/22/05	0.63	1.74	99.2
9/22/05	0.76	1.53	98.9
9/27/05	0.47	1.81	99.2
9/27/05	0.58	1.74	98.9
	Mean: 0.65 SD: 0.13 %RSD: 19.3%	Mean: 1.83 SD: 0.45 %RSD: 24.5%	Mean: 98.2 SD: 2.0 %RSD: 2.1%

### 3.3 VOCs.

Figure 12 depicts a sample chromatogram obtained after analyzing the smoke tubes collected from a given sampling day, along with an atmospheric blank and field blank overlaid on the same set of axes, detected by GC/MS. Only the concentrations of compounds varied between disseminations, depending on the total concentration that was present in the sampling shed. Qualitative detection of the compounds did not vary. Most of the compounds from the disseminations were long straight chained hydrocarbons (C40, C50, C60 chains) and had retention times of 10 min or greater. Other smaller chained hydrocarbons were observed but at much lower concentrations. Some of the other compounds observed were sulfur dioxide, hexamethylcyclotrisiloxane, xylene, octamethylcyclotetrasiloxane, dl-limonene, and thionosulfites. All of these compounds had early retention times ( $< 8$  min) except for the thionosulfites which had retention times of nearly 25 min. There were no polynuclear aromatic hydrocarbons detected in the disseminated smoke. All compounds present in the field blank and atmospheric blank were predominantly long straight chained hydrocarbons.

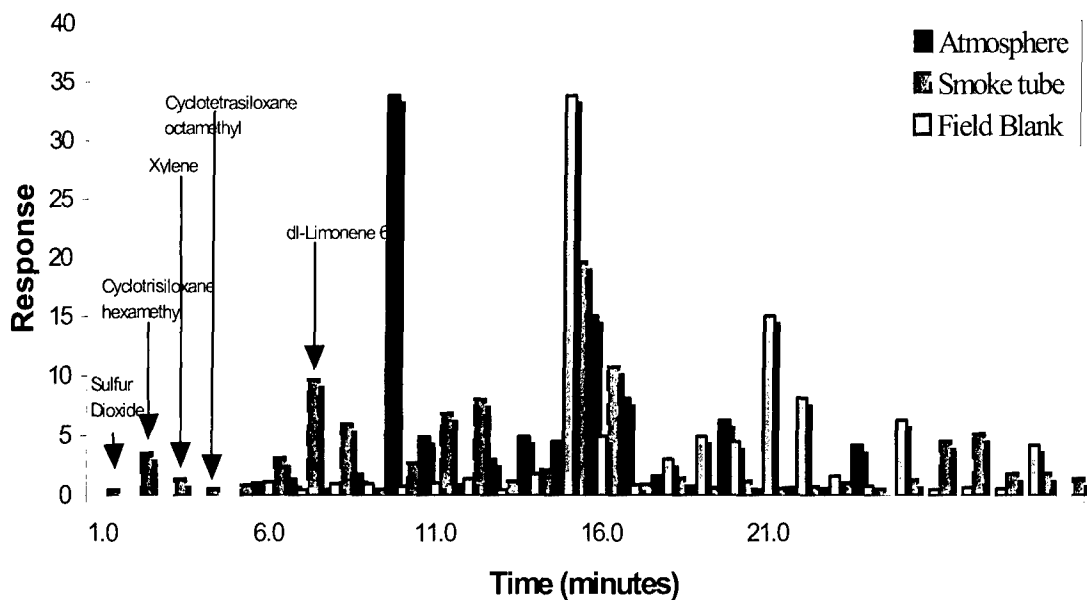


Figure 12. GC/MS Chromatogram of Atmospheric Blank, Field Blank, and Sample Tube Taken from Shed

### 3.4 Inorganic Gases.

Carbon monoxide, sulfur dioxide, nitrogen oxides, and formaldehyde were the only inorganic gases found above their detection limits on the colorimetric detector tubes. The highest observed concentration for carbon monoxide was 10 ppm, sulfur dioxide was 1.8 ppm, nitrogen oxide was 12.5 ppm and formaldehyde was 15 ppm. No other inorganic gases were found in the disseminated smoke.

### 3.5 Inorganic Anions.

#### 3.5.1 Inorganic Anions - Standards and Calibration.

An example chromatogram for a 50:1 dilution of the anion primary stock solution is shown in Figure 13. Figure 14 gives calibration curves for five of the seven anions. A curve for bromide and chloride were not provided because they were not anticipated to be seen for these tests. The limit of detection for each anion was determined to be 0.2, 0.006, 0.04, 0.03, and 0.006 mg/L for phosphate, fluoride, sulfate, nitrite, and nitrate, respectively (S/N = 3).

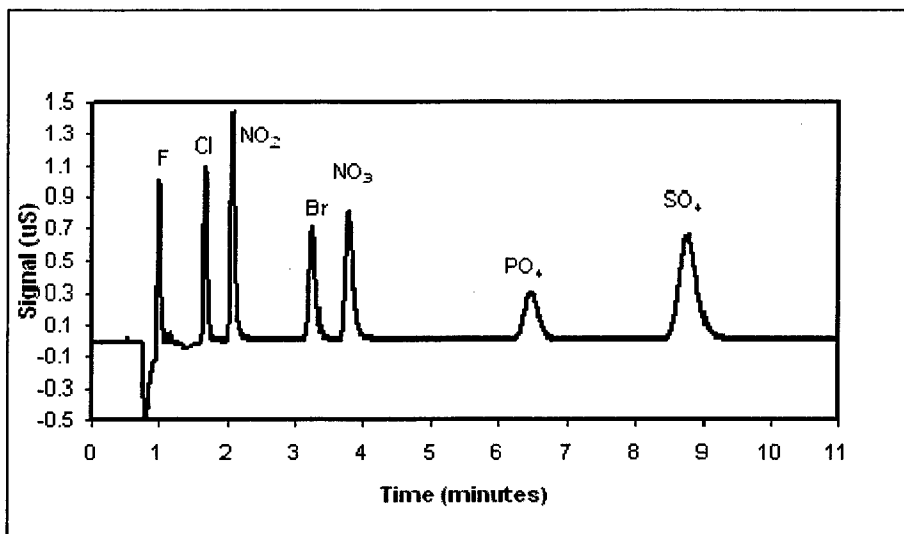


Figure 13. Chromatogram of Anion Standard Diluted 50 Times. Separation by anion exchange with suppressed conductivity.

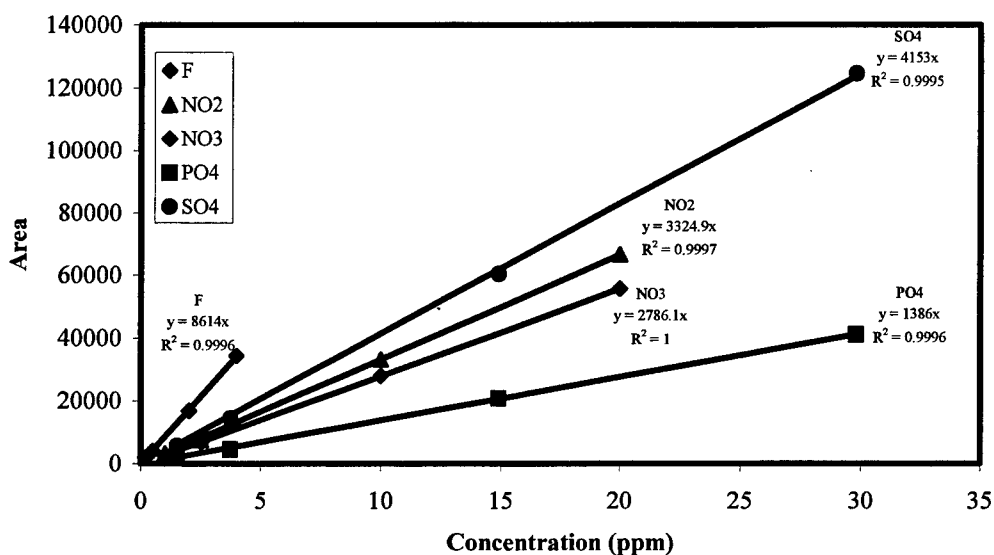


Figure 14. Calibration Curve for Anions by Area Separated by IC with Suppressed Conductivity Detection

### 3.5.2 Inorganic Anions - GFF Pads.

Extraction efficiencies were measured by amending known concentrations of phosphate standard onto blank GFF pads. The IC mobile phase (1.7 mM NaHCO<sub>3</sub> / 1.8 mM Na<sub>2</sub>CO<sub>3</sub>) was used for solvent extraction. Extraction efficiencies were >90% for concentrations  $\geq 100$  ppm.

Phosphate was the main anion found in the samples. The total weight on the GFF pads and the analytically determined weight of phosphate on the pads are given in Table 5. From this, the percentages of smoke residue that were comprised of phosphate were calculated and shown in Table 5 and graphically in Figure 15.

Table 5. Percentage of Phosphate Material within the KM03 Disseminated Aerosol

Day	Weight on GFF PAD (mg)	Phosphate (mg)	% Phosphate on Pad
8/18/05	16.38	10.27	62.71
	12.00	7.58	63.18
	16.45	10.49	63.79
	30.34	14.83	48.87
8/24/05	86.08	59.96	69.65
	77.31	53.50	69.20
	78.56	55.20	70.26
	184.00	136.46	74.17
8/25/05	51.58	35.51	68.84
	62.8	42.66	67.94
	64.93	44.64	68.75
	181.64	135.35	74.52
9/1/05	129.57	95.18	73.46
	104.01	74.91	72.03
	105.76	100.16	94.70
9/19/05	177.60	56.28	31.69
	177.50	127.47	71.82
	88.6	56.64	63.93
9/27/05	51.54	34.41	66.76
	99.71	63.99	64.18
	103.87	68.17	65.63

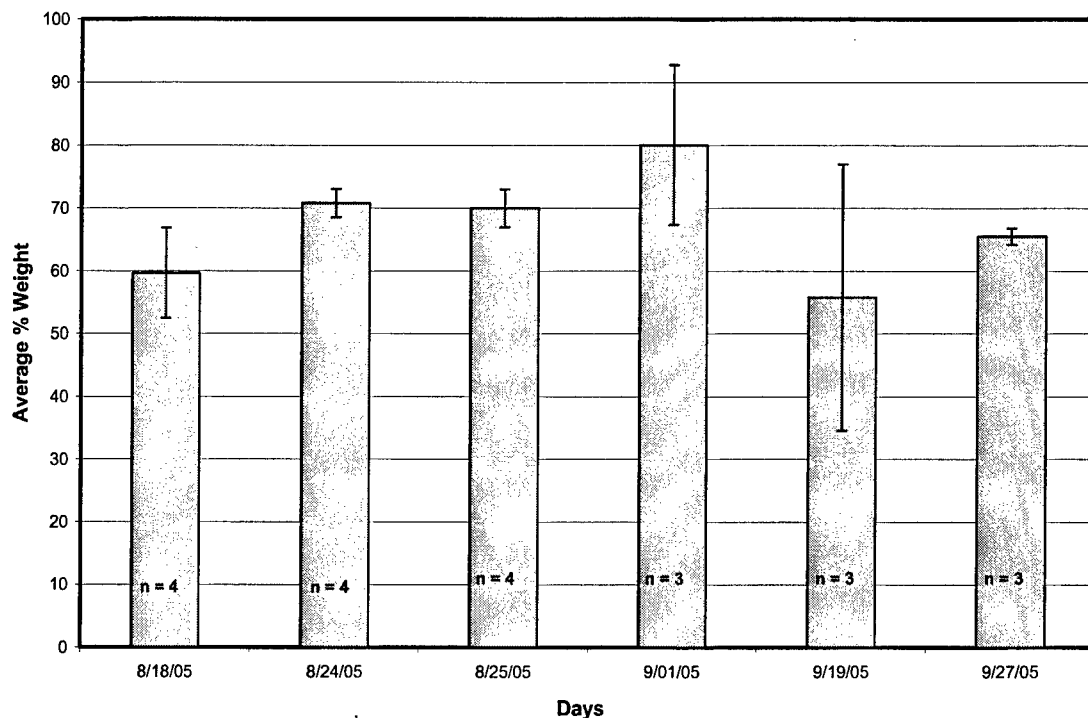


Figure 15. Percent Weight for Phosphate Determined on GFF Pads

### 3.6 Inorganic Cations.

#### 3.6.1 Inorganic Cations - Standards and Calibration.

Figure 16 provides an example of a cesium calibration curve. The correlation coefficient ( $r^2$ ) was  $>0.999$  and the limit of detection was determined to be 0.07 mg/L (S/N = 3).

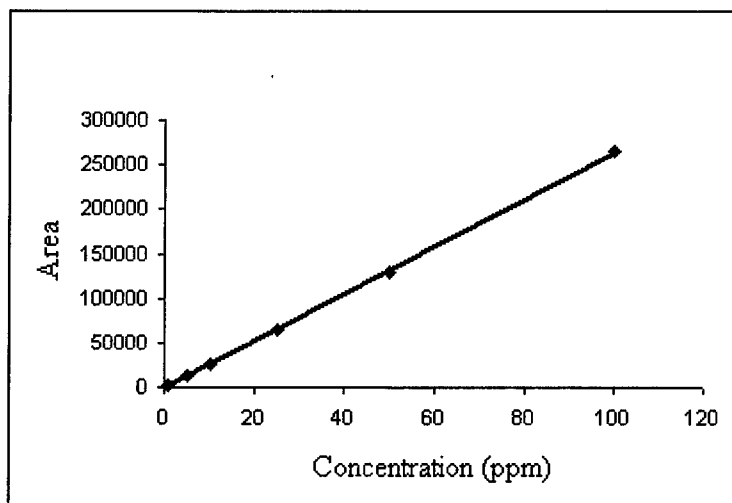


Figure 16. Calibration Curve for Cesium Separated by IC with Suppressed Conductivity Detection

### 3.6.2 Inorganic Cations - GFF Pads.

Extraction efficiencies were measured by amending known concentrations of cesium standard onto blank GFF pads. Deionized water was used for solvent extraction. Extraction efficiencies were >90% for concentrations  $\geq 0.1$  ppm.

Cesium was the main cation found in the samples. The total weight on the GFF pads and the analytically determined weight of cesium on the pads are given in Table 6. From this, the percentages of smoke residue that were comprised of cesium were also calculated and provided in the table.

Table 6. Percentage of Cesium Material within the KM03 Disseminated Aerosol

Day	Weight on GFF PAD (mg)	Cesium (ug)	% Cesium on Pad
8/18/05	30.34	55.03	0.18
8/24/05	184.0	228.66	0.12
8/25/05	181.64	101.63	0.06
9/1/05	105.8	113.13	0.11
	104.01	69.22	0.07
	129.57	91.26	0.07
9/19/05	88.6	93.26	0.11
	84.3	44.65	0.05
	177.5	80.31	0.05
	177.6	78.33	0.04
9/27/05	51.54	76.62	0.15
	99.71	146.28	0.15
	103.87	166.23	0.16

### 3.7 Aquatic Toxicology.

Point estimation of  $EC_{50}$  calculations (the effective concentration that immobilizes 50% of the organisms) were performed using the Trimmed Spearman-Kärber method.<sup>26</sup> The  $IC_p$  (the concentration that causes a 50% inhibition of offspring production or growth) was calculated using a linear interpolation methods for calculating inhibition concentrations.<sup>27</sup>

Survival and reproduction data were subjected to hypothesis testing, to determine the No Observable Effects Concentration (NOEC) and the Lowest Observable Effects Concentration (LOEC). Survival data were subjected to Fisher's Exact test to determine if there were any significant survival differences at the 95% confidence level between control and treatment groups. Reproduction data were subjected to One Way Analysis of Variance (ANOVA) to determine significant differences at the 95% confidence level among control and treatment groups. The Bonferroni's Multiple Comparison test was used to determine which



treatment groups were statistically different from the control. If the data did not pass the test for homogeneity, the nonparametric Steel's Many-One Rank Test was used. The statistical tests were performed using Toxstat.<sup>28</sup> Treatment groups having no survival in any replicates were excluded from the NOEC and LOEC reproduction calculations. However, the treatment groups having no survival were included in the calculation of the EC<sub>50</sub> and IC<sub>p</sub> endpoints.

### 3.7.1 Microtox (MTX) Assay.

Using the ZnSO<sub>4</sub> standard, and the culture-lot of *Vibrio fischeri* used in this investigation, all QA/QC results fell within the acceptable range for ZnSO<sub>4</sub> EC<sub>50</sub> values (between 3 and 10 mg/L) for 15-min exposure MTX bioassays. The MTX bacteria were exposed to smoke residue extracts up to 2,512 mg/L. The 5 min EC<sub>50</sub> = 782.3 mg/L (95% CI, 400.0 – 1528.3 mg/L) and the 15 min EC<sub>50</sub> = 712.3 mg/L (95% CI, 388.8 – 1305.0 mg/L).

### 3.7.2 Algal Assay (*Selenastrum capricornutum*).

The green algae (*Selenastrum capricornutum*) were subjected to floating smoke pot residue extract up to 2000 mg/L. Algal growth was stimulated 14 and 11 % (compared to the control) in treatment groups 125 and 500 mg/L respectively (Figure 17). However, this was not biologically significant (level of significance 95%). Algal growth was significantly inhibited when exposed to smoke residue extracts of 2000 mg/L, which resulted in a 33% cell growth inhibition. The Lowest Observable Effects Concentration (LOEC) was 2000 mg/L and the No Observed Effects Concentration (NOEC) was 1000 mg/L. Therefore the IC<sub>50</sub> (concentration that inhibited cell growth to 50% of the control cell growth) could not be determined. However, the IC<sub>20</sub> = 1040 mg/L (95% CI, 444.1 – 1298.1 mg/L)

### 3.7.3 Ceriodaphnia Assay (*Ceriodaphnia dubia*).

The control ceriodaphnia met the EPA test acceptability criteria of  $\geq 80\%$  survival and producing an average of 15 or more young per adult. There was 100 % mortality after 48 hr of exposure to 1004 mg/L residue extract, with 50 % mortality in the 502 mg/L treatment group after 7 days. The 7-day EC<sub>50</sub> = 502 mg/L (95% CI = 403.2 – 625.0 mg/L ) while the 48 hr EC<sub>50</sub> = 662 mg/L (95% CI = 580.8 – 755.5). The Lowest Observable Effects Concentration (7-D LOEC) was 251 mg/L and the No Observable Effects Concentration (7-D NOEC) was 126 mg/L (Table 7). The IC<sub>50</sub> (the inhibitory concentration that reduced reproduction to within 50% of the control) and IC<sub>20</sub> were 218 mg/L (95% CI = 202.1 to 236.3) and 156.2 mg/L (95% CI = 142.4 to 165.2 mg/L) respectively.

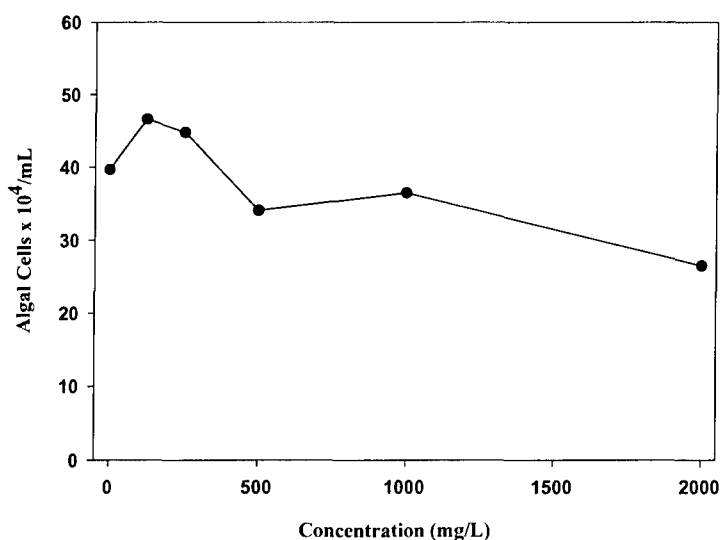


Figure 17. Algal (*Selenastrum capricornutum*) Growth after 96 Hr of Exposure to Smoke Residue Extract

Table 7. Effects of RP Smoke Residue on *Ceriodaphnia dubia* Reproduction

Concentration (mg/L)	Survival (%)	Mean Young Production
Control	100	24.6
16	100	24.6
32	100	24.6
63	100	24.2
126	100	23.3
251	100	*8.3
502	*50	
1004	*0	

\* Significantly Different (significance level 95%)

### 3.8 Long-Term Storage Test.

#### 3.8.1 Long-Term Storage Test Results.

Samples of air (2 L) taken from the climatically controlled chamber were analyzed by the colorimetric tube method (Kitegawa, phosphine detector tube Part Number 8014-121SD) and by GC/MS. A calibration curve for phosphine was generated using the GC-MS method with the 5 ppm phosphine/air standard. Concentrations of 500 to 50 ng were determined to be linear as shown in Figure 18. The slope was determined to be 43.95 with a correlation coefficient ( $r^2$ ) of 0.9979. The limit of detection was determined to be 25 ng. An air volume of 250  $\mu$ L was used for injections onto the GC/MS. There was no phosphine detected in

the samples at or above the detection limit either by the colorimetric tubes or by the GC-MS methods.

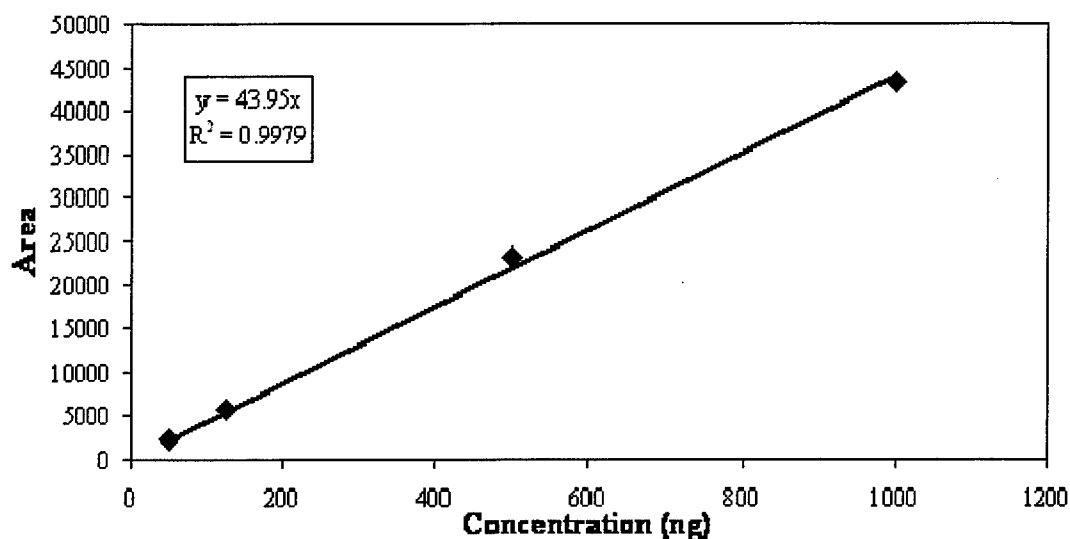


Figure 18. Calibration Curve for Phosphine Detected by GC/MS

### 3.8.2 Post Long-Term Storage.

Following the smoke pot long-term storage (prior to cooling) it was observed that the lid to hobcock 4 was bulged outward (Figure 19). The chamber was allowed to cool and the smoke pots were stored until disseminated. After the cooling process had completed, the walls of the hobcocks for smoke pots 1-3 were observed to be pushed inward, but the walls and lid of hobcock 4 were observed to be normal.



Figure 19. Top of Smoke Pot #4 Indicating Where the Smoke Pot Lid is Bulged Out

## 3.8.3

Sampling from Post Long-Term Storage FSP.

Samples were taken from the “dead volume” inside the hobbocks from the floating smoke pots in order to determine if phosphine had been produced and trapped inside the hobbock. The samples were taken by drilling a hole through the hobbock into the lower portion of the dead space (Figure 20 grayed in area, approximately 11 L) between the hobbock and smoke pot (see Hole #1 Figure 20) (Note: when the drill bit broke through the wall of the hobbocks on smoke pots 1-3, a rush of air was heard entering the hobbock, the walls immediately went back to their original configuration, and their walls were no longer pushed inward). This was not observed with pot 4. A 2-L syringe was then sealed to Hole #1 with duct seal and Hole #2 (see Hole #2 Figure 20) was drilled into the upper portion of the dead space but on the opposite side of Hole #1. Immediately upon Hole #2 being drilled, 1-L air sample was taken from the dead space with the syringe. After collecting the air sample, the hobbock was opened, the smoke pot was removed and disseminated.

Results from the dead volume inside the hobbocks of the long-term storage floating smoke pots are provided in Table 8. Both the designated ECBC numbers and corresponding original Diehl numbers are provided. The table shows that very high concentrations of phosphine were found inside the hobbocks of all four smoke pots as compared to the TLV-TWA for phosphine, 0.3 ppm. The sample from smoke pot #3 unfortunately leaked before determining the actual concentration. A separate air sample from a smoke pot not subjected to long term storage was also taken and analyzed as a control. Phosphine was not detected using the colorimetric detection method for the blank but approximately 5 ppm of phosphine was detected by GC/MS.

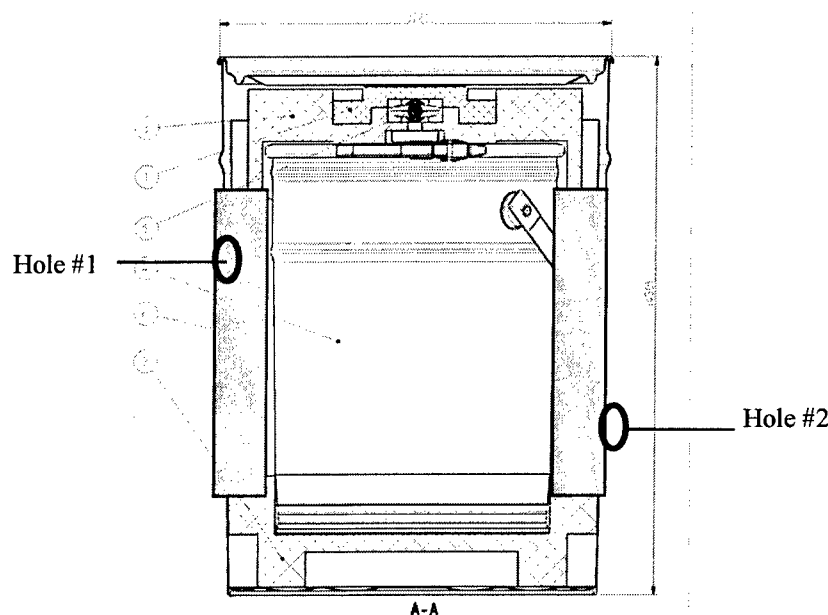


Figure 20. Schematic of Inside Smoke Pot and Location of Hole Drilled to Sample the Dead Volume

Table 8. Phosphine Detected in Post Long-Term Storage for FSP 1-4

Smoke Pot # (ECBC, Diehl)	Average Concentration PH <sub>3</sub> Detector Tube (ppm)	Injection Volume (mL)	Average Concentration GC-MS (ppm)
No Long Term Storage	n/d	0.1	5.27
1, 77	2800-3000	0.01	2604.66
2, 72	1000-1500	0.05	1590.96
*3, 7	100-150	0.005	128.0
4, 21	>7000	0.005	9779.30

\* Sample leaked and escaped

After collecting samples for phosphine gas, the four pots were disseminated to determine whether they functioned the same as the pots that were not artificially aged. All pots functioned normally, burned for approximately 22-24 min, and all burned the same percentage of the smoke payload as compared with the pots not artificially aged.

#### 4. DISCUSSION

##### 4.1 Particle Size.

Small particle sizes are not uncommon for disseminated materials that are pyrotechnically generated. A mean MMAD of 0.65  $\mu\text{m}$  implies that the particles will likely undergo impaction in the alveolar portion of the lower respiratory system.<sup>29</sup> With this particle size, it is likely that diffusion mechanisms at the blood barrier will not occur but deep deposition into the respiratory system is still probable. Further evidence is provided by the high mean percentage (98%) of particles that were found to be respirable ( $\leq 3\mu\text{m}$ ). Respirable is defined by the ACGIH as particles that are deposited in the gas-exchange alveolar region of the lung.

In many instances, particle size analyses may reveal two distinctive MMAD's, and thus infer a bimodal distribution.<sup>30-32</sup> Some particles may be generated from condensations and tend to be small while other larger particles are generated by shearing and other mechanical forces that work on the parent material. This is seen because combustion and pyrolysis inherently produce a tremendous amount of energy. Typically, the lower mode is in the 1  $\mu\text{m}$  range but bimodality is usually reflected in larger  $\sigma_g$ 's of around 3. The current study returned a  $\sigma_g$  of 1.83, thereby providing evidence that the distribution is not bimodal.

During dissemination of the KM03 smoke pot, a 1-2 ft flame accompanied the tests. At the conclusion of the test, it was observed that there was virtually no solid fallout present either in the collection shed or on any of the sampling equipment. The absence of fallout material also suggests that the process is conducted at extremely high temperatures. Due to the high heat and associated turbulence, larger particles are therefore not formed as aggregates.

Long chained aliphatic alkanes (>20 carbons) are compounds traditionally seen from the dissemination and combustion of smoke materials. In the smoke produced from the KM03 smoke pots, n-tetracontane (C40), n-pentacontane (C50), n-hexacontane (C60), and n-octacontane (C80) were observed. To separate these compounds by GC/MS, elevated temperatures were necessary for the movement of these compounds through the analytical column and their subsequent identification with mass selective detection. Identification of the individual aliphatic compounds was confirmed by the distinctive fragmentation patterns observed. Typically, straight chain alkanes are rather simple to elucidate from the consistent loss of 14 atomic mass units (amu's). This weight loss corresponds to the loss of numerous methylene (-CH<sub>2</sub>) groups in the compounds. Quantitation of these hydrocarbon compounds along with other smaller hydrocarbons was unnecessary because their observed levels were not of toxicological significance.

Siloxane was also found in the GC/MS chromatograms for the VOC's. Generally, siloxane is associated with tenax "bleed" due to the higher temperatures required for the complete analysis of the VOC's collected. Limonene, xylene, and sulfur dioxide were also detected in small quantities during the disseminations. Usually, limonene occurs naturally in trees, bushes, and/or citrus oils, but its reason for its presence in the characterized smoke is unclear. Xylene is a dimethyl substituted benzene compound that was also identified from the mass spectrometry library. Unlike benzene, which has a TLV-TWA of 0.5 ppm, the regulated exposure level for xylene is much higher (TLV = 100 ppm). The levels of xylene observed from the KM03 smoke pots were much lower than this and were therefore not of toxicological concern. Sulfur dioxide was also observed at low concentrations, which was confirmed through the colorimetric tubes used during the inorganic gas analysis. No PAH compounds were detected in the disseminated smoke.

Following each dissemination, the air sample was analyzed for inorganic gases that were all considered to be possible combustion products. Table 9 lists the Threshold Limit Values-Time Weighted Averages (TLV-TWA'S) and the toxicological effect for the inorganic anions and gases analyzed. Some compounds listed in the table are also reported using a Short Term Exposure Limit - Ceiling (STEL-C). The values are as listed by the American Conference of Governmental Industrial Hygienists (ACGIH).<sup>33</sup> Carbon monoxide was observed during the disseminations but did not exceed its established TLV. Formaldehyde levels observed within the combusted smoke (2-15 ppm) did exceed the TLV-STEL of 0.3 ppm but its source of formation is unknown. The highest levels of sulfur dioxide (1.8 ppm) were nearly equivalent to the established TLV-TWA of 2 ppm. The NO<sub>x</sub> tubes are an EPA standard that simultaneously measures for nitric acid (NO) and nitrogen dioxide (NO<sub>2</sub>). During combustion processes, the primary pollutant is the free radical form of NO. Usually, conversion occurs in tens of minutes to NO<sub>2</sub>. By the way in which the experiment was designed, most of the NO<sub>x</sub> was probably in the form of NO<sub>2</sub> by the time the air was analytically sampled. The highest concentrations of NO<sub>x</sub> measured were 12.5 ppm. Although the TLV-TWA for NO was not exceeded, the TLV-TWA

of 3 ppm for NO<sub>2</sub> was exceeded. A short term exposure would be the most likely form of exposure, but, it must be noted that samples were taken at a distance of 7-8 ft from the smoke pot. It would be anticipated that formaldehyde, sulfur dioxide and nitrogen oxide concentrations would increase at shorter distances. As expected, phosphine was not detected during the normal disseminations.

Table 9. TLV-TWA and Toxicological Effects for Inorganic Anions and Gases

Anion/Gas	TLV-TWA (ppm)	Effect
Phosphoric Acid	0.25	irritation
Sulfuric Acid	0.05	mucostasis
Nitric Oxide	25	irritation
Nitrogen Dioxide	3	irritation
Phosphine	0.3	irritation
Fluoride	3.2	irritation
Ammonia	25	irritation
Carbon monoxide	25	Anoxia, *CVS,**CNS
HCN	10	CNS, irritation
Formaldehyde	0.3 (STEL-C)	irritation, cancer
Sulfur dioxide	2	irritation
HCl	2 (STEL-C)	irritation, corrosion

\*CVS – CardioVascular System

\*\*CNS – Central Nervous System

#### 4.4 Inorganic Anions - GFF Pads.

The mean concentration of phosphate (principally in the form of phosphoric acid) calculated over the last five dissemination dates was 513 ppm with a standard deviation of 221 ppm. The overall range was 322-740 ppm. Although this is much higher than the established TLV for phosphoric acid (0.25 ppm), the presence of high amounts of phosphoric acid in these smokes must be expected. However, even with dissipation, the high concentrations observed in the fine particle mist could still induce an irritancy effect in personnel. This effect is common with all RP based smokes.

The amount of phosphate determined by IC in milligrams comprised a large portion of the total weight found on the GFF pads (milligrams). The amount of phosphate extracted from the pad was proportional to the amount of material that was collected on the pad. Statistical analysis was done by ANOVA with a Bonferroni-Dunn post-test. The 95% confidence level was used as the criterion for statistical significance. All data sets were found to have no significant difference between the percentage weight of phosphate.

#### 4.5 Inorganic Cations - GFF Pads.

The mean concentration of cesium calculated over the study was 0.40 ppm with a standard deviation of 0.19 ppm. The overall range was 0.21-0.59 ppm. The current established TLV-TWA for cesium hydroxide is 0.3 ppm. The amount in micrograms of cesium found on the pad was proportional to the amount of material that was collected on the pad. According to the possible reaction pathways, one possible scheme involved the combustion of cesium nitrate to form cesium hydroxide, which is of toxicological concern to the ACGIH and NIOSH. The ion chromatography method utilized in the current study measures the total cesium that is present in the aerosol residue. This would include cesium hydroxide as well as additional combustion products of cesium that may be formed. Although the experimental mean value exceeds the TLV, the standard deviation implies that it is not significant. This along with the suggestion that other cesium compounds other than cesium hydroxide might be included in the calculation provides confidence that the production of cesium compounds do not pose a substantial risk during disseminations.

The amount of cesium found (micrograms) was small compared to the total weight found on the GFF pads (milligrams). The amount in micrograms of cesium found on the GFF pads was proportional to the amount of material that was collected on the pad. Statistical analysis was done by ANOVA with a Bonferroni-Dunn post-test. The 95% confidence level was used as the criterion for statistical significance. Using the respective means, the only data set found to be significantly different between each other was 19 Sep 05 and 27 Sep 05. All other data sets found no significant difference between the percentage weight of the cesium.

#### 4.5 Aquatic Toxicology.

Results from the definitive aquatic toxicity assays showed that the green alga *S. capricornutum* was the least sensitive organism to RP Floating Smoke Pot residue among the three species tested. Although the toxic effects to algae is low (stimulated growth up to 14% at low concentrations), the indirect effects should not be overlooked. As indicated by slight growth stimulation at low concentrations, one possible indirect effect is the increased risk of algal blooms. Algal blooms increase the risk of dissolved oxygen depletion which can lead to eutrophication of aquatic habitats.

The toxicity results from the extracted smoke residue from the RP Floating Smoke Pot were scored using the Chemical Scoring System for Hazard and Exposure Identification.<sup>34</sup> This system is typically used in the preliminary screening process, and is not intended to be a substitute for Environmental Risk Assessments. The system assigns a score based on the acute and/or chronic toxicity data. When multiple species data are available, the scoring is to be based on the most sensitive species and within that species, the most sensitive criteria (acute or chronic NOEC data) should be used.

The scoring system developed by O'Bryan and Ross scores toxicity using EC<sub>50</sub> and chronic NOEC values.<sup>34</sup> This system is based on scoring criteria from 0 to 9, 9 being the most toxic. However this system does not rank the scores using common terms typically used in mammalian toxicity rankings. The U.S. Fish and Wildlife Service (USFWS) published a



Research Information Bulletin suggesting relative aquatic toxicity terms based on EC<sub>50</sub> data.<sup>35</sup> The ranking system considers EC<sub>50</sub> results >1000 mg/L to be “Relatively Harmless” and results less than 0.01 mg/L as “Super Toxic.” Similar descriptive rankings are used by Kamrin.<sup>36</sup> In this study the ceriodaphnia were the most sensitive species, having an NOEC value of 126 mg/L verses the 48 hr and 7d EC<sub>50</sub> values of 662 and 502 mg/L respectively. The toxicity of the RP smoke residue received a score of 3 (Practically Nontoxic, based on the Ceriodaphnia NOEC value), see Table 10.

Table 10. Most Sensitive Criteria (Ceriodaphnia NOEC) Used in Determining the Smoke Residue Score/Ranking

Test Species	Toxicity Criteria	Score	Ranking
<i>Vibrio fischeri</i>	5 min EC <sub>50</sub> = 782.3 mg/L	1	Practically Nontoxic
	15 min EC <sub>50</sub> =712.3 mg/L	1	Practically Nontoxic
<i>Selenastrum capricornutum</i>	96 hr EC <sub>50</sub> > 2000 mg/L	0	Relatively Harmless
	NOEC = 1000 mg/L	0	Relatively Harmless
<i>Ceriodaphnia dubia</i>	48 hr EC <sub>50</sub> =662 mg/L	2	Practically Nontoxic
	7 Day EC <sub>50</sub> = 502 mg/L	2	Practically Nontoxic
	NOEC = 126 mg/L	3	Practically Nontoxic

#### 4.6 Long-Term Storage Test.

Artificial aging that simulates long-term storage of munitions is accomplished by using the Arrhenius relationship. Currently, it offers the only mechanism of aging besides natural aging. As with nearly all chemical reactions, the reaction rate may be increased with increasing temperature. Higher temperatures inherently promote a higher probability of two molecules colliding and subsequently reacting.

In many instances, it is desirable to determine whether “older” units will function, or in this case, it was desirable to additionally determine whether phosphine gas would evolve over time. With many of the RP munitions, phosphine evolution is a known phenomenon that occurs during storage. The current smoke pot employed new encapsulation technology that was developed to address the issue of phosphine evolution. The formation of phosphine is a simple bimolecular reaction between phosphorous and water (typically from air humidity) to form phosphine gas and oxygen. Phosphine is considered very toxic by inhalation. The current 60 min LC<sub>50</sub> value for phosphine is 20 ppm. Phosphine may also accumulate in confined spaces, especially at or below ground level, with low concentrations producing poor warning properties. It is also known to form explosive mixtures in air. Currently, the lower explosive limit (LEL) of phosphine is 1.6% (16,000 ppm).<sup>14</sup>

During the test, there was no phosphine detected in the chamber down to the limits of detection for both analytical methods. There are several plausible explanations for phosphine not being present inside the chamber. First, phosphine is slightly more dense than air and might have settled to the bottom of the chamber; however the constant circulation of the

chamber air should prevent any localized accumulation of phosphine. Secondly, phosphine is considered highly reactive and could have reacted with the air between sampling intervals and formed phosphoric acids. This reaction would be more prevalent in an environment with increased percentages of relative humidity.<sup>14</sup> In the current test, the elevated temperatures produced an environment with low humidity ( $\leq 5\%$ ), thereby making this conversion to phosphoric acid unlikely.

High concentrations of phosphine gas were detected in the "dead" volume space between the smoke pot and the hobcock. For all of the pots tested, two analytical methods were used to confirm concentrations. The colorimetric tubes are a quick concentration determination while the GC/MS method is a more analytically accurate method. Concentration values determined for each pot correlated well for the two methods. The concentration level observed for pot 4 is believed to be the most accurate. When the first hole was drilled into the outer hobcock on pots 1-3, an audible pressure difference was heard, thereby inferring a rapid influx of dilution air from the outside air and into the hobcock. The concentration that was built up within hobcock 4 after the long-term storage was nearly 10,000 ppm and the allowable TLV- TWA is 0.3 ppm. Future investigation should be performed to evaluate this observation and determine methods to possibly alleviate these elevated levels of phosphine.

#### 4.7 Comparison of FSP to HC Smoke Pots.

Toxicity comparisons need to be made between the replacement RP FSP to previously reported data on the M4A2 HC smoke pot. Determinations may then be made to assess whether toxicological improvements have been made towards satisfying the original program's KPP of developing a lower toxicity smoke.

In hexachloroethane pots, smoke is produced by burning a mixture containing roughly equal parts of hexachloroethane:zinc (II) oxide and approximately 6% granular aluminum.<sup>6</sup> Exposures to HC smoke have been shown to induce death attributed to respiratory insufficiency due to edema of the lungs or acute respiratory distress syndrome.<sup>6</sup> Dissemination causes an exothermic, self perpetuating combustion reaction that produces zinc (II) chloride, solid carbon, and aluminum oxide.<sup>6</sup> Upon cooling, the zinc chloride forms an aerosol that rapidly absorbs water from the surrounding atmosphere. The acute toxic effects of exposure to HC smoke that have been reported are considered to arise primarily from inhalation of the zinc chloride component. Zinc chloride is corrosive and astringent and known to cause burning of moist body surfaces including the respiratory and gastrointestinal tract; has been reported to damage nerve endings in the nasal passages; and to cause eye burns damaging smell and vision.<sup>6</sup> The absence of these smoke components alone in the current FSP formulation suggests a reduced toxicity risk as compared to the HC smoke pots.

Chloride is a predominant anion that is produced during the dissemination of HC smokes. On introduction into the air, it may be presumed that chloride quickly may convert into hydrochloric acid (HCl). This is the same reasoning for the subsequent conversion of phosphate to phosphoric acid in the current study. The ACGIH Short Term Exposure Limit (STEL) for HCl is 2 ppm while the current STEL for phosphoric acid ( $\text{H}_3\text{PO}_4$ ) is 0.74 ppm. This would imply that the STEL for  $\text{H}_3\text{PO}_4$  is nearly three times less than the STEL for HCl. However the

concentrations of HCl recorded for the HC pots ranged from 3,000-19,000 ppm<sup>6</sup>, while the concentrations for phosphoric acid observed in the current study were 322-744 ppm. These higher concentrations of HCl may also be expected because HC smoke pots were considered to be an excellent, dense producing obscurant. The STEL for phosphoric acid is less than hydrochloric acid, but the concentration of hydrochloric acid produced from the HC smoke pots is considerably higher than the concentration of phosphoric acid produced from the FSP's. The respiratory irritancy effect introduced from HCl in HC smoke could then be thought to be greater than the irritancy effect introduced from H<sub>3</sub>PO<sub>4</sub> for the FSP.

The MMAD's reported for the HC pots have ranged from 0.4 to 2.8 µm.<sup>6</sup> Unlike the FSP, bimodality of the particle size is inferred with the HC pots where experimental evidence might suggest the presence of two distinct MMAD's. In the current FSP, the mean particle size (MMAD) was 0.65 µm, with no experimental evidence for bimodality. For the HC and FSP pots, sampling was conducted at a similar distance from the point of dissemination and they both utilized similar collection equipment. As with the FSP's, the HC smoke pots would still have a majority of the particles considered respirable but the particles would be spread out more within the areas of the upper and lower respiratory tract because of the wider range of sizes. From a human health perspective, it might be suggested that both would be unfavorable because nearly all of the particles are considered respirable.

The VOC's detected in the current study from the disseminated smoke have been discussed and were toxicologically insignificant, as compared against the respective TLV's. Some VOC's were analyzed in the HC smoke pots and they also were not observed to introduce additional toxicity problems. Inorganic gases do not appear to be of high concern for both types of smoke pots. However, extremely high levels of phosphine (above the TLV-TWA) were detected during long term storage of the FSP's. No comparable data was available for the HC smoke pots.

Fisher et al.,<sup>37</sup> conducted a study using a synthetic mixture of Hexachloroethane (HC) Smoke residue. The synthetic formulation was based on the analysis of HC smoke residue conducted by the U S Army Medical Research and Development Command.<sup>37,38</sup> The synthetic HC residue consisted of ten components. Of these, tetrachloroethylene, aluminum oxide and zinc chloride made up 86% of the residue. The 100% nominal concentration of the residue used in Fisher's study was 63.1 mg/L. This study used nine freshwater organisms which included fish, macroinvertebrates, and green algae. The most sensitive species tested were *Selenastrum capricornutum* (Green Algae), *Salmo gairdneri* (Rainbow trout), and *Daphnia magna* (water flea) which had EC<sub>50</sub> values of <5.6, 2.2, and 9.3 % respectively. This data was transformed to milligrams per liter (Table 11) based on the nominal concentration of 63.1 mg/L, to allow for data comparison to the RP smoke pot residue toxicity.

Based on the toxicity of HC synthetic smoke residue to algae, the HC residue was approximately 570 times more toxic than the RP FSP residue. The overall toxicity score for synthetic HC smoke residue was 7 (Moderately Toxic). The known presence of heavy metal oxides such as aluminum, lead, arsenic, iron, and cadmium within HC smoke also contribute heavily towards the overall aquatic toxicity score. In comparison, the overall toxicity score for the RP smoke was determined to be 3 (Practically Nontoxic).

Table 11. Aquatic Toxicity of Synthetic HC Smoke Residue

Test Species	Toxicity Criteria	Score	Ranking
Green algae	96 hr EC <sub>50</sub> < 3.5 mg/L	7*	Moderately Toxic
Rainbow trout	96 hr EC <sub>50</sub> = 1.4 mg/L	7	Moderately Toxic
Water flea	48 hr EC <sub>50</sub> = 5.8 mg/L	6	Moderately Toxic

\* 3.5 mg/L of HC residue caused a 99.6% reduction in alga growth, if a definitive EC<sub>50</sub> were determined, the toxicity score could possibly be much higher.

This information provides a direct comparison of the toxicity of smoke residues, however, the actual concentration of residue that would be deposited during deployment of smoke is unknown. Information is needed on the down range deposition and how the residue components may react with naturally dissolved material in an aquatic ecosystem before any type of environmental assessment can be conducted.

## 5. CONCLUSIONS

Obscurants have historically been important to the military in various applications. The development and creation of safe and effective smokes and obscurants is of great importance to the U.S. Military. One important point to emphasize is that there is no smoke formulation that is considered non-toxic. The role of development is to create the "safest" smoke formulation possible that would retain operational efficiency. The Floating Smoke Pot (FSP) MK 7 MOD 0 Program was established to redesign the previously fielded M4A2 Hexachloroethane (HC) FSP. Potential human health and environmental risks associated with the RP smoke pot have been evaluated by making comparisons against limits established by regulatory agencies. Also comparisons have been made to previously reported data on the M4A2 HC smoke pot and have shown that the newly designed RP-FSP shows toxicological improvements over the HC smoke pot and as such satisfies the KPP of developing a low toxicity smoke.

The data suggests red phosphorous (RP) floating smoke pots do not create additional risks upon dissemination, and the products are generally found to be less hazardous than for the HC smokes. Combustion products, inorganic anions and cations, particle size, volatile organic compounds, and aquatic toxicology were all evaluated. The greatest concern for the current replacement smokepot program would be the high levels of phosphine that were observed during long-term storage.

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